URITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

REPORT SECURITY CLASSIFICATION none	1b. RESTRICTIVE MARKINGS none
SECURITY CLASSIFICATION AUTHORITY none	3. DISTRIBUTION / AVAILABILITY OF REPORT unlimited
DECLASSIFICATION / DOWNGRADING SCHEDULE none	
PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report # 65	5. MONITORING ORGANIZATION REPORT NUMBER(S) ONR N00014-89-J-1225
NAME OF PERFORMING ORGANIZATION University of Southern Mississippi	6b. OFFICE SYMBOL (If applicable)
7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Department of Polymer Science Hattiesburg, MS 39406-0076	7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 North Quincy Street Arlington, VA 22217-5000
NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
ADDRESS (City, State, and ZIP Code) Chemistry Division 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK ACCESSION

AD-A282 326

1. TITLE (Include Security Classification)

Thianthrene-Based Poly(benzoxazole)s

2. PERSONAL AUTHOR(S)

R. A. Johnson, L. J. Mathias

3a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 6/1/93 TO 5/31/94	7/15/94	

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

DTIC
ELECTE
JUL 25 1994
S F

19. ABSTRACT

See attached.

94-23191

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	
22a. NAME OF RESPONSIBLE INDIVIDUAL Leon J. Mathias	22b. TELEPHONE (Include Area Code) 601-266-4871
	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

1994

THIANTHRENE-BASED POLY(BENZOXAZOLE)S

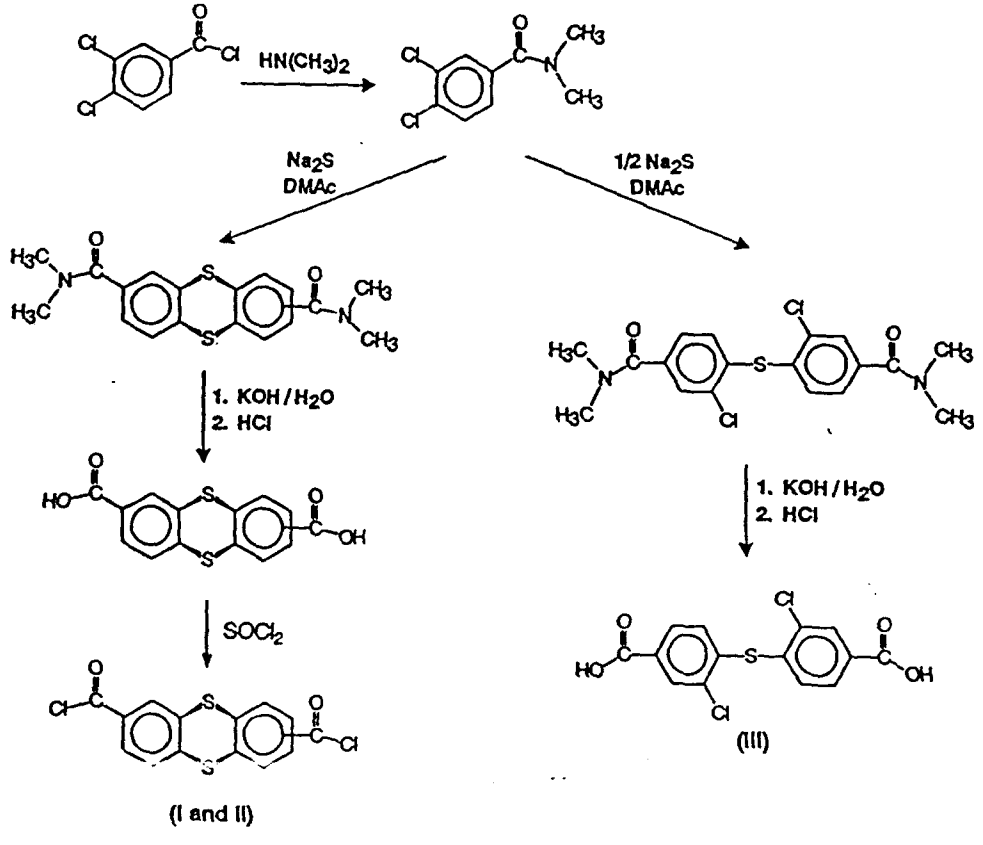
Randy A. Johnson and Lon J. Mathias*
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

INTRODUCTION

Poly(benzoxazole)s (PBOs) are a class of rigid-rod polymers that are known to have good thermal stability, high mechanical properties, and environmental resistance. Processing of PBOs is difficult since they have low solubility, high glass transition temperatures, and decompose before their melting points.

This study is focused on improving the processibility of poly(benzoxazole)s by increasing their solubility while maintaining good thermal stability. With this goal in mind, we synthesized thianthrene-based PBOs from thianthrene-2,7- and -2,8-dicarbonyl chlorides with commercially available bis-o-aminophenols. Polymers were prepared in poly(phosphoric acid) at 90-200 °C. Transparent PBO films were casted from polymerization solutions and m-cresol depending on solubility. Thermal analysis has shown 10% weight loss in air at > 500 °C. DMA has shown good mechanical properties with a transition > 400 °C for polymer I-HAB.

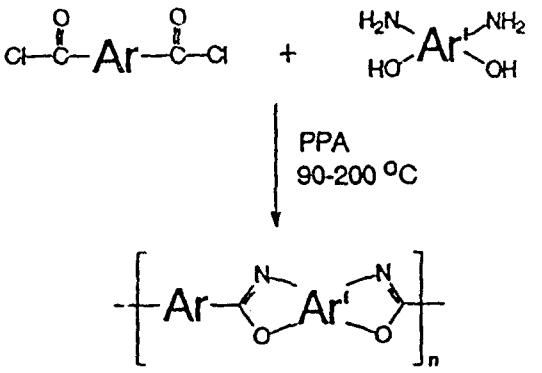
Synthesis of Thianthrene-2,7- and -2,8-dicarbonyl chlorides



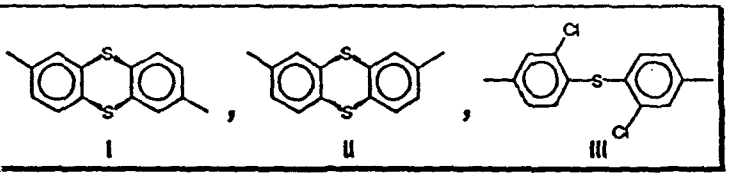
(I and II)

(III)

Poly(benzoxazole) synthesis

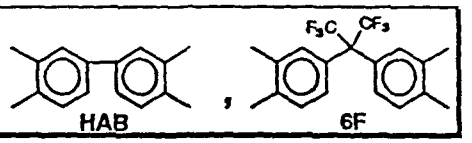


Ar =

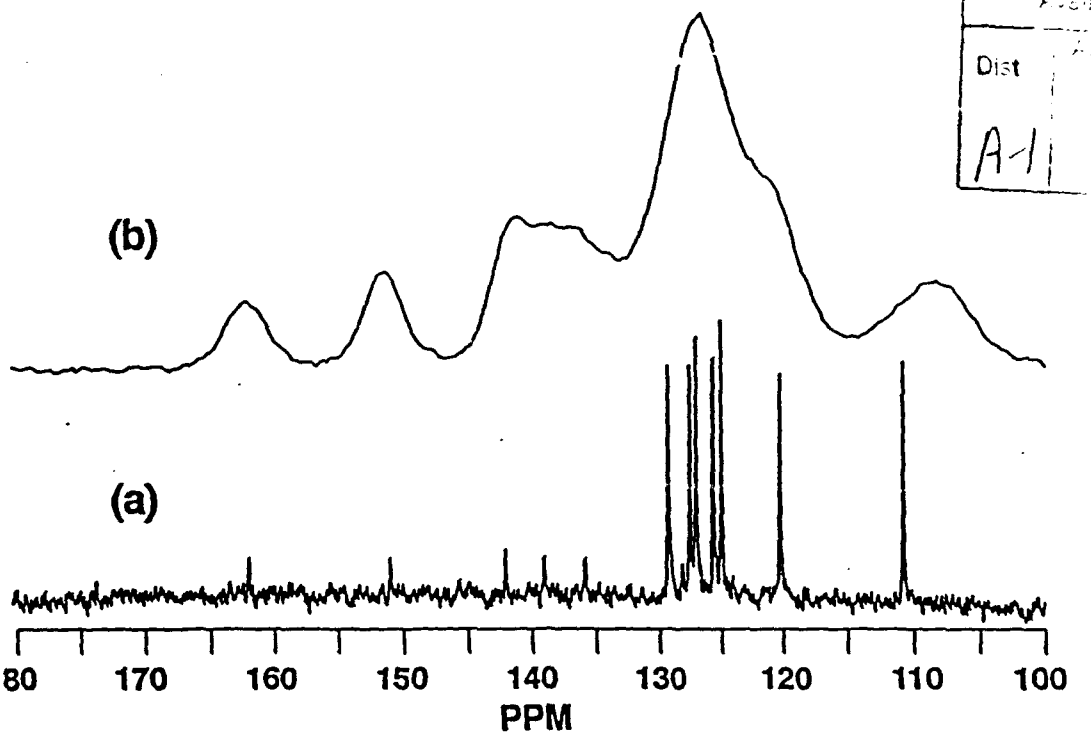


I , II , III

Ar' =



HAB , 6F



^{13}C NMR of (a) 2,7-bis(2-benzoxazolyl)thianthrene (model) and (b) thianthrene-biphenyl PBO (I - HAB) in $CDCl_3$ and solid state, respectively.

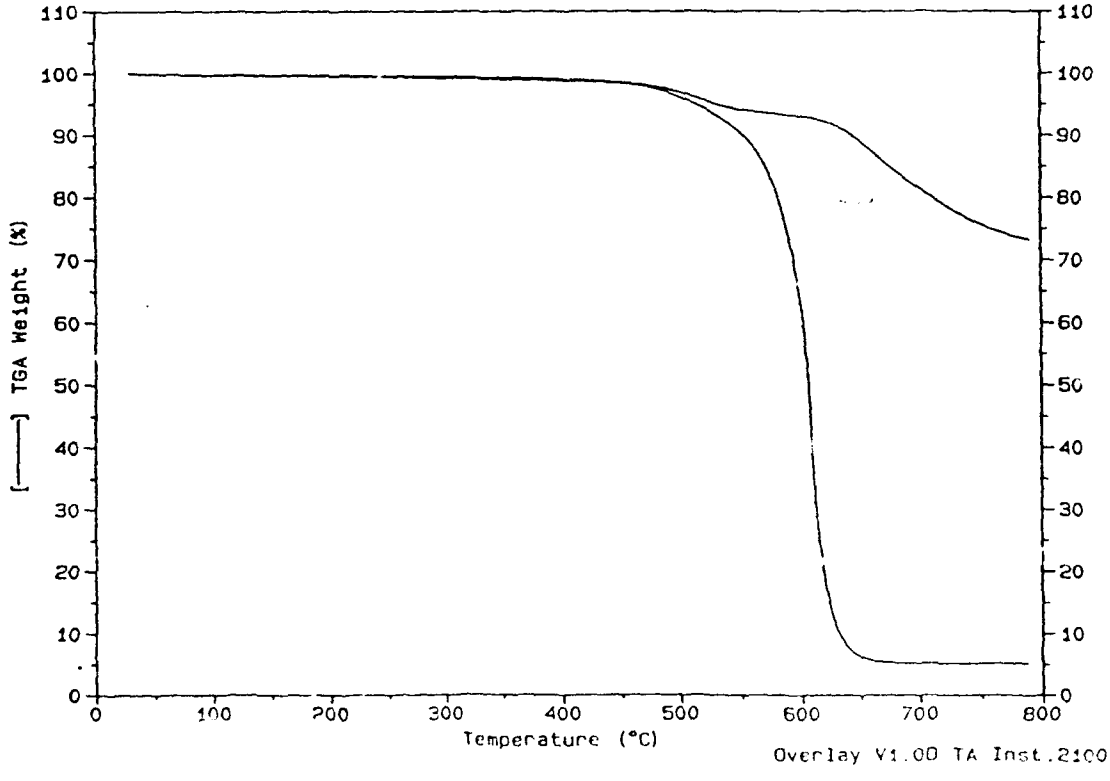
POLYMERS	H_2SO_4	$MeSO_3H$	m-cresol	$CHCl_3$	THF	dichloro-benzene	$MeNO_2$[a] $AlCl_3$
I - HAB	b	b	–	–	–	–	–+
I - 6F	++	++	++	–	–	–+	++
II - HAB	b	++	–	–	–	–	++
II - 6F	++	++	++	–	–	–+	++
III - HAB	++	++	–	–	–	–	++
III - 6F	++	++	++	–+	–	++	++

[a] 18 wt% $AlCl_3$.
b Partially soluble.
++ Soluble at ambient temperature.
–+ Soluble hot.
– Insoluble.

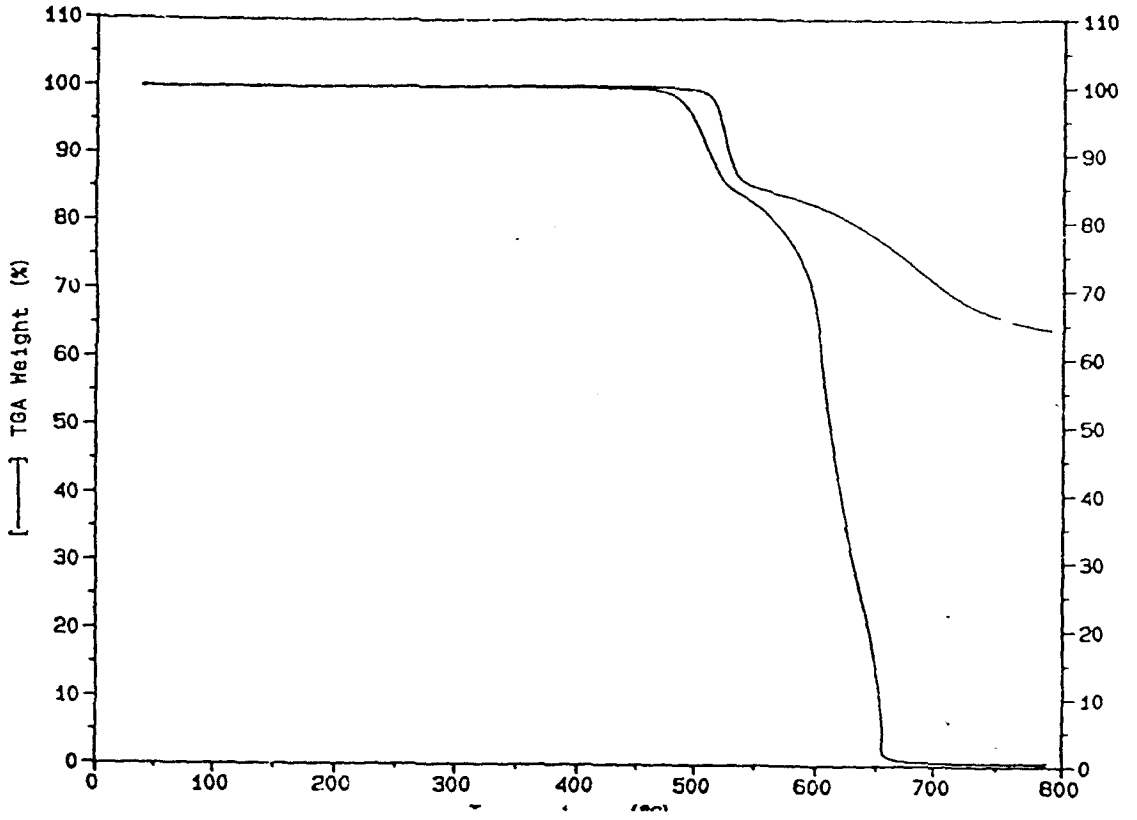
POLYMERS	η_{inh} (dL/g)	TGA[b] (°C)	
		onset temp. (N_2 / air atm.)	10% wt. loss (N_2 / air atm.)
I - HAB	–	451 / 450	643 / 551
I - 6F	0.92[a]	478 / 455	533 / 528
II - HAB	–	462 / 391	655 / 590
II - 6F	1.51[a]	435 / 442	545 / 526
III - HAB	–	473 / 459	533 / 511
III - 6F	0.88[a]	453 / 449	500 / 488

[a] Measured in m-cresol at 30 °C.
[b] Measured at heating rate of 10 °C/min.

TGA of PBO I-HAB in nitrogen (upper trace) and air (lower trace).



TGA of PBO III-HAB in nitrogen (upper trace) and air (lower trace).



DMA of PBO I-HAB.